Reply to "Comment on: 'A recoupled states approximation for molecular scattering theory' "

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We would like to thank Dr. Hahne[1] for pointing out a term we overlooked in the exact Lippmann–Schwinger equation. The calculations in Ref. 2 were done using the differential equation. Perhaps an approximation of the sort Dr. Hahne proposed could be developed. The recoupled states approximation as it stands gives an improvement in the inelastic cross sections over the coupled states approximation and gives slightly worse elastic cross sections than coupled states.

A cursory reading of our paper[2] on the recoupled states approximation may give the impression that it fails more often than it is correct. We gave many examples of conditions under which the approximation was bad and only one example for which it was good. This is perhaps an overreaction to the ubiquitous papers in the literature describing a new approximation and showing only examples in which it works beautifully and leaving the reader in the dark as to the region of validity of the approximation. We give a very thorough exposition of the limits of validity of the recoupled states approximation allowing one to make a reasonable estimate as to the validity of the approximation in any particular case. We note that when the recoupled states approximation fails the coupled states approximation also fails, and when both approximations fail the recoupled states still give better inelastic cross sections than coupled states.

When the coupled states approximation is good, the recoupled states approximation gives essentially exact results, when coupled states is bad, recoupled states is good and when coupled states fails completely, recoupled states is only marginally better. Since recoupled states is a correction to coupled states the size of the correction gives an indication of the validity of both approximations.

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(1+ 1) CDAD: A new technique for studying photofragment alignment

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In recent years, the alignment of photofragments created by photodissociation of polyatomic molecules has been under intense investigation.[1–4] Alignment information provides insight into the dynamics of the photodissociation process. Until now, fluorescence techniques (most often laser-induced fluorescence or LIF) have been used almost exclusively to determine the photofragment alignment.[1–4] In this Comment we report a new method for probing photofragment alignment, namely, circular dichroism in the photoelectron angular distributions (CDAD).[5,6] Most importantly, we demonstrate here that the photofragment alignment can be extracted from the CDAD spectra in a straightforward manner, *independent* of the photoionization dynamics. We believe this characteristic should enhance the practicality of this technique. CDAD has recently been observed experimentally.[7] Here, we only give the highlights of this new method: the details will be given in a later publication.[8]

The (1 + 1) CDAD experiment involves excitation of the photofragment with linearly polarized light to an electronically excited state followed by photoionization with left or right circularly polarized light.[5,6] To simplify the description of the experimental arrangement, we assume the dissociation laser and excitation laser to be the same. The CDAD experiment is then performed as follows: Through the molecular sample, the linearly polarized dissociation/excitation pump laser is co-/counterpropagated with the circularly polarized probe laser. The polarization vector of the pump laser is rotated by a polarizer. A photoelectron detector is *fixed* in the plane at right angles to the propagation directions of the lasers. Angular distributions are obtained as a function of θ, the angle between the pump polarization direction and the photoelectron collection direction.

The difference between the photoelectron angular distributions obtained using left and right circularly polarized light is called the CDAD spectrum.[5,6] In a recent paper,[6] we

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have shown that the CDAD spectrum has the simple form

$$I(\theta) = \sum_L a_L P_L^1(\cos\theta), \tag{1}$$

where

$$a_L = A_L \overline{\beta}_L. \tag{2}$$

Here, A_L is the state multipole moment describing the *excited state* alignment and $\overline{\beta}_L$ is a J-dependent quantity (where J is the total angular momentum of the excited state) which contains dynamical information about the photoionization process.[5,6] For a photofragmentation reaction in which the ground state alignment of the photofragment is described solely by A_0' and A_2'[9] (primes for the ground state), L in Eq. (1) can take two values, 2 and 4.

The ground state photofragment alignment is typically characterized by one parameter $A_0^{(2)}$[9] which is related by a simple formula to the ratio A_2'/A_0'.[3] To obtain $A_0^{(2)}$ with CDAD, one measures the (1 + 1) CDAD spectra for two different branches, i and k, and determines the ratio $R = a_2^i/a_2^k$ [a_2 from Eq. (1)]. The ground state alignment is then given simply by

$$A_0^{(2)} = \frac{(M_0^i - M_0^k R)}{(M_2^i - M_2^k R)}. \tag{3}$$

The M's have general analytical forms which are too lengthy to express or derive here.[8] We specialize them here for the (1 + 1) scheme in NO, $X\,^2\Pi \xrightarrow{h\nu} A\,^2\Sigma \xrightarrow{h\nu}$ ion (Table I). The E values in the table are the one-photon relative line intensities for the different branches which are given in analytical form for a $^2\Pi \rightarrow {}^2\Sigma$ transition by Earls.[10] to get the M values for a mixed branch ($P_{21} + Q_{11}$ for example) one simply adds the M values (with the correct values of E) for the individual branches. We emphasize that these expressions are *not* classical limits but rather a result of lengthy algebraic evaluation of 3J, 6J, and 9J symbols.

Why does Eq. (3) look so simple? The answer is that the β_L in Eq. (2) can be factored into a J-dependent part (with 3J and 6J symbols) and a dynamical part *independent* of J.[8] The latter part cancels in the ratio R so that the dynamical information about the photoionization process is removed from Eq. (3). The M's also contain the angular momentum algebra necessary to convert the excited state alignment created by one-photon absorption back into the ground state alignment (neglecting saturation effects). Simple expressions for the M's as in Table I should be obtainable for other molecules and other transition schemes as well.

Which branches should be chosen to determine $A_0^{(2)}$? It will be shown elsewhere[8] that P and R branches exhibit the greatest CDAD effect when $A_0^{(2)}$ is negative, while Q branches show the greatest effect when $A_0^{(2)}$ is positive. Since the value of $A_0^{(2)}$ is to be determined, a few branches should be checked to find two suitable for use in Eq. (3). Our calculations indicate that the maximum CDAD intensity in favorable branches will be about 20% of the intensity at 0° of the left (or right) spectrum. This is well within the current experimental capability.[7] Measurements of photofragment alignment of NO by (1 + 1) CDAD are currently underway.[11]

TABLE I. M expressions for (1 + 1) CDAD through the $A\,^2\Sigma$ state of NO (Hund's case b). Here J is the total angular momentum of the photofragment *initial* state. E is described in the text.

Branch	M_0	M_2
P	$E\frac{(2J-3)}{J}$	$E\frac{25(J+1)(2J-3)}{7J(2J-1)}$
Q	$-E\frac{(2J-1)(2J+3)}{J(J+1)}$	$E\frac{5(11J^2+11J-15)}{7J(J+1)}$
R	$E\frac{(2J+5)}{(J+1)}$	$E\frac{25J(2J+5)}{7(J+1)(2J+3)}$

For NO photofragments in the $^2\Pi$ ground state, uneven population of Λ doublet components (Π^+ and Π^-) in each of the manifolds ($^2\Pi_{1/2}$ and $^2\Pi_{3/2}$) is possible.[1,3,4] This effect can be unraveled in a straightforward manner, requiring only the relative intensities of the left (or right) spectra at $\theta = 0°$ for a few specific branches. The CDAD spectra themselves are not even required. Unwanted contributions to the photoelectron signal from pump laser ionization can likewise be accounted for by similar measurements at $\theta = 0°$. Ionization by the pump laser can also be clearly suppressed by choosing an (n + 1) CDAD scheme. Details will be published elsewhere.[8]

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